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# Formation of liquid and solid products from liquid phase pyrolysis

N. Schwaiger [a,*], V. Witek [b], R. Feiner [a], H. Pucher [a], K. Zahel [b], A. Pieber [b], P. Pucher [b], E. Ahn [b], B. Chernev [c], H. Schroettner [c], P. Wilhelm [c], M. Siebenhofer [a]

[a] *Institute of Chemical Engineering, Graz University of Technology, Inffeldgasse 25/C, 8010 Graz, Austria*
[b] *BDI-BioEnergy International AG, Parkring 18, 8074 Grambach/Graz, Austria*
[c] *Institute for Electron Microscopy, Graz University of Technology, Steyrergasse 17, 8010 Graz, Austria*

## HIGHLIGHTS

- Liquid phase pyrolysis is a process dedicated to biochar and biocrudeoil production.
- The process is not very sensitive to particle size.
- During pyrolysis the lignin frame stays almost substantially stable.
- Lignin frame undergoes just sintering and shrinking.
- Liquid and solid product formation is almost finished after 800 s.

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## ABSTRACT

The aim of the present work was to improve the C:O ratio in biomass by preserving the lignin macrostructure of lignocellulosic feed. The intention of liquid phase pyrolysis is to liquefy biomass and prepare biomass for further upgrading steps like hydrogenation and deoxygenation. Pyrolysis was carried out in a non-aqueous liquid phase heat carrier. The process was carried out in a semi-batch reaction vessel under isothermal conditions at $T = 350\ ^\circ C$, supported by a quench to stop reactions instantaneously in order to observe formation of solid intermediates. This pyrolysis system enables the observation of liquid and solid product formation. Transformation of biomass into biochar was analyzed by infrared spectroscopy and elemental analysis. Stable lignin structure throughout the whole transformation was confirmed. It was shown that the lignin frame in wood remains without substantial loss, while the major amount of carbohydrates is pyrolyzed during liquid phase pyrolysis at $T = 350\ ^\circ C$.

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## 1. Introduction

Despite of improved exploring and production methods, fossil fuels are obviously vanishing. OPEC (2008, 2011) discloses at the end of the year 2011 1.2 billion barrels of proven crude oil reserves, compared to 1.7 billion barrels of reserves at the end of the 1980s. This demonstrates a strong decrease of reserves and this is just a result of retarding peak oil with highly developed exploration techniques. Even though nowadays exploration is coupled with higher risks, as the Deepwater Horizon disaster showed in April 2010. Parallel to decreasing crude oil resources climate change is a global threat. To avoid rising world average temperature and to become independent of overseas energy imports the European Union (EU-Directive, 2008) wants to reduce greenhouse gas emissions according to the European Directive (2009) by 20% and raise the percentage of renewable fuels up to 10%. To limit imports of crude oil and reduce greenhouse gasses, biofuels are a promising alternative. First generation biofuels like biodiesel and bioethanol are ready to market technologies, but with a limited range of feasibility, caused by the specific needs of energy crops. Moreover first generation biofuels are affected by negative food versus fuel discussion in mass media. To avoid this discussion biodiesel industry tries to turn feedstock from edible plants to non-edible feedstock like algae biodiesel. Open or closed pond systems for algae production are probably feasible alternatives (Tredici and Zittelli, 1998; Richmond, 2000) but at the moment there are still many obstacles to face (Früwirth, 2010).

A serious alternative to these routes to liquid fuels is the thermo-chemical conversion of lignocellulosic material. The most important reason is the availability, by ecologic treatment of this resource. “It is estimated that the total phytomass of earth is $1.24 \times 10^{12}$ metric tons and 80% of which is attributed to wood. The potentially utilizable annual wood growth is $1.1 \times 10^{10}$ ton”

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[*] Corresponding author.
*E-mail address:* nikolaus.schwaiger@tugraz.at (N. Schwaiger).

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(Nimz et al., 2000). There are two major pathways to apply liquefaction of lignocellulose. First the Fischer–Tropsch technology, which was used by "Choren GmbH" or the "Karlsruhe Institut für Technologie". This technology is based on first step gasification of biomass to synthesis gas (Choren, 2007) or indirect biomass gasification of pyrolysis oil and biochar slurry to synthesis gas (Dinjus, 2010), coupled with Fischer–Tropsch reaction in a second step. On the one hand gasification combined with Fischer–Tropsch reaction is, with respect to the biomass feed, a highly flexible path for production of high level quality fuels (Rauch, 2010). On the other hand this technology needs enormous cost of investment.

The second path is the direct Biomass liquefaction which is well described in literature (Bridgwater et al., 1999; Meier and Faix, 1999; Carlson et al., 2008; Demirbas, 2001; Di Blasi et al., 1999; Mohan et al., 2006). There are various applications like fixed bed reactors, entrained flow reactors, rotating cone reactors mentioned in literature. The range of reaction temperature for optimum liquid product yield is between 450 and 600 °C (Huber et al., 2006). Highest liquefaction output of 75–80% is obtained with fast pyrolysis between 450 and 550 °C and a very short residence time (Bridgwater and Peacocke, 2000).

### 1.1. Liquid phase pyrolysis

In addition to fast pyrolysis and Fischer–Tropsch synthesis liquid phase pyrolysis is dedicated to form solid and liquid products. Products of liquid phase pyrolysis are noncondensibles, biocrude oil, and biochar. Liquid phase pyrolysis improves the C:O ratio of lignocellulose during biomass conversion, leaving the lignin frame unaffected. Liquid phase pyrolysis generates water and pyrolysis oil with low inorganics load. Operation temperature and product yield classify liquid phase pyrolysis between fast pyrolysis and torrefaction as shown in Table 1: Comparison of several pyrolysis systems; torrefaction (Prins et al., 2006), slow pyrolysis (Williams and Besler, 1996), fast pyrolysis (Gerdes, 2001) and liquid phase pyrolysis. Detailed information about liquid phase pyrolysis is reported elsewhere (Schwaiger et al., 2011).

## 2. Methods

### 2.1. Reactor design

The reactor was designed according to the needs of fed batch operation. The schematic is shown in Fig. 1. Biomass was fed through a 40 mm ball type inlet valve. Heat carrier was agitated with 150 rpm. All condensibles were condensed in a water cooled heat exchanger tube. Set point of vapor temperature at the condenser outlet was 15 °C. Inert atmosphere was provided by two nitrogen feed lines. The temperature was controlled in the liquid heat carrier phase, in the vapor phase above the heat carrier, at the condenser inlet and at the end of the condenser. For determination of kinetics a second cask was fixed at the biomass outlet valve. This cask was separately purged with nitrogen to provide inert atmosphere and it was cooled with ice water.

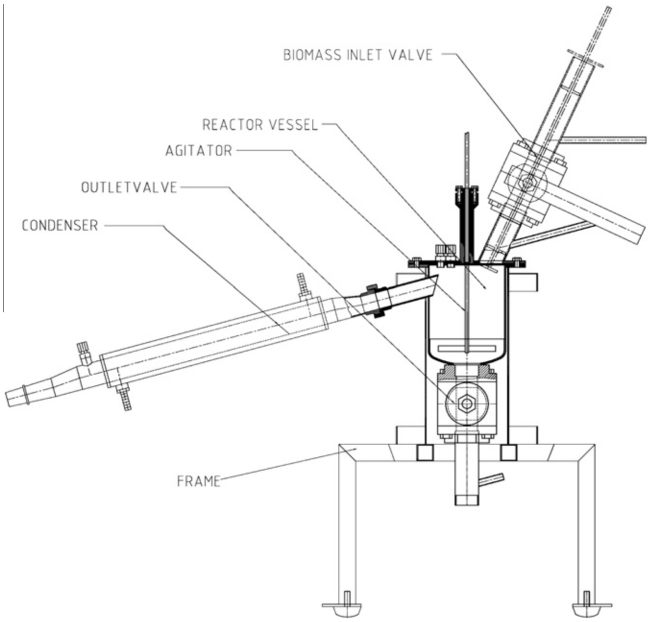

**Fig. 1.** Schematic of the reactor.

### 2.2. System

Biomass was pyrolyzed in liquid heat carrier at ambient pressure. The heat carrier was a highly hydrogenated mixture of straight long chain alkanes. Elemental composition of the heat carrier was 86% carbon and 14% hydrogen. The liquid heat carrier provided sufficient heat conductivity (~0.100 W/m K at $T = 350$ °C) and high heat capacity of ~2.4 kJ/kg K at $T = 350$ °C for isothermal operation of semibatch pyrolysis. The heat carrier was a mixture of *n*-alkanes, with a boiling range between 410 and 440 °C. The total amount of heat carrier in the reaction vessel was 500 g. After 1 h and 20 min of preheating, the reactor temperature of 350 °C was reached.

For kinetic experiments 17 g of biomass was then added under nearly isothermal operation conditions. The temperature change was ±2 °C during metering of biomass. Due to the limited influence of particle size on liquid phase pyrolysis, wood-cubes with a diameter of 10 mm were used and the wood-cubes were cut with a band saw. Formation of liquid products was monitored by weight.

Biochar formation in the heat carrier was stopped by quenching in the ice cooled cask. An immediate drop of temperature to less than 150 °C was obtained by mixing the product with precooled heat carrier in excess.

Feedstock for kinetic experiments for this study was bone-dry spruce wood, to avoid formation of heterogeneous azeotropic mixtures of excess water and the heat carrier. Biomass, spruce wood cubes with a particle size of 10 × 10 × 10 mm, was dried for 24 h at 105 °C. In a first series of experiments lignin, hemicellulose and cellulose were separately pyrolyzed. 100 g of each compound was pyrolyzed in 500 g of heat carrier. The lignin (alkali lignin

**Table 1**
Comparison between several pyrolysis systems.

| Parameter | Torrefaction (Prins, 2006) | Slow pyrolysis (Williams, 1996) | Fast pyrolysis in a fluidized bed reactor (Gerder, 2001) | Liquid phase pyrolysis |
|---|---|---|---|---|
| Temperature [°C] | 300 | 300 | 476 | 350 |
| Liquid yield [wt%] | 28 | 28 | 67.4 | 40–44 |
| Char [wt%] | 60.8 | 66.8 | 16 | 37–40 |
| Gas [wt%] | 11.2 | 5.2 | 16.6 | 13–16 |

CAS 8068-05-1, $M_w$: 28000 g/mol from Sigma–Aldrich), hemicellulose (birchwoodxylan $M_{(132)n}$ from Carl Roth GmbH) and cellulose powder (CAS 9004-34-6 from Sigma–Aldrich) were also dried for 24 h at 105 °C. The Biomass was added in six portions of 16.6 g every 5 min under nearly isothermal operation conditions. The temperature change was ±2 °C during metering of biomass compounds. During pyrolysis biocrude oil was entrained with heat carrier because of formation of heterogeneous azeotropes due to limited miscibility of biocrude oil, water, and heat carrier.

### 2.3. Analytics

The gas flow rate was recorded by red-y gas flow meter (Vögtlin). Gas composition was analyzed by a Madur Photon II infrared gas analyzer for $CH_4$, $O_2$, CO and $CO_2$.

All liquid and solid products and educts were characterized by elemental analysis with a Vario macro CHNO-analyzer, from Elementar Analysensysteme, in CHN mode. In addition the liquid products were analyzed by GC–MS[1] 5890 Series, Hewlett Packard, with a WCOT fused silica 30 m low bleed column. The heat carrier and entrained heat carrier composition were determined with a GC-SimDis[2] MXT 2887, 10 m column from Restek and Agilent 7890A GC. Water was measured with GC-TCD[3]. After the experiment the heat carrier and biochar were separated by filtration in a first step and afterwards biochar was refined in a second step by solid/liquid extraction with hexane for 24 h in a Soxhlet apparatus. ATR-FTIR[4] measurements of Biochar were performed by Graz Center of Electron microscopy with an Equinox 55 FTIR spectrometer, connected to a Hyperion 3000 IR microscope. The used objective was an ×20 ATR-objective with germanium crystal with flattened tip (approx. 100 μm width). ESEM[5] Photos were taken with a FEI Quanta 200 ESEM by Graz Center of Electron microscopy.

## 3. Results and discussion

At 350 °C Liquid phase pyrolysis of lignocellulose provided two mayor products; pyrolysis oil and biochar. The overall mass balance was 40–44% liquids, 37–40% biochar and 13–16% gaseous products at $T = 350$ °C. At maximum 3% of liquid yield was dissolved in the liquid heat carrier. Biochar yield of liquid phase pyrolysis was rather comparable with intermediate pyrolysis reactor systems than with fast pyrolysis (Enders et al., 2012).

### 3.1. Formation of liquid and solid products

A first test of liquid phase pyrolysis without admixture of biomass gave a constant condensed heat carrier flow due to evaporation as shown in Fig. 2 marked as line a. The flow rate was dependent upon the ambient pressure being between 0.002 and 0.004 $g_{\text{Heat carrier}}$/s.

During pyrolysis, evaporable reaction products like water and liquid CHO-products formed heterogeneous azeotropes with the heat carrier. The overall liquid product stream consisted of evaporated heat carrier, azeotropic entrained heat carrier, water and liquid CHO-products. Kinetics of overall condensibles is shown in Fig. 2 line b.

By subtracting the evaporated heat carrier stream (Fig. 2 line a from Fig. 2 line b), the reaction dependent flow of azeotropic entrained heat carrier, water and liquid CHO-products was isolated. Fig. 2 line c shows the kinetics of liquid product formation. From these results a three step process is proposed:

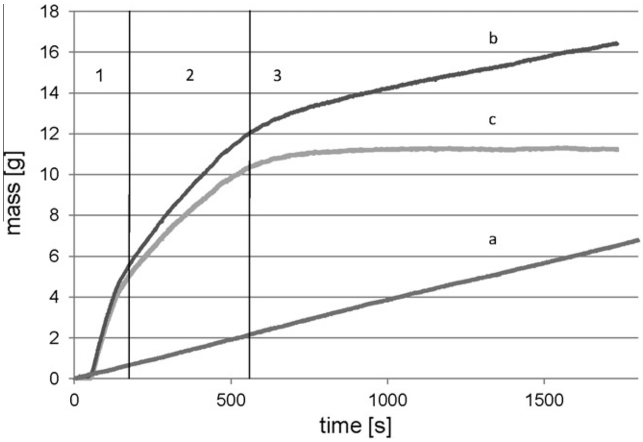

**Fig. 2.** Liquid product formation.

1. Dewatering in a first phase.
2. Liquid product formation in a second phase.
3. Stagnation of conversion without any further liquid product formation in a third phase.

Investigation of pyrolysis kinetics of spruce wood considered different particle size of the feed between 630 μm and wood cubes with a lateral length of 10 mm. Rate of formation of condensibles did not show any dependency of product formation and particle size. Seemingly heat transfer to the core of particles and diffusion of degradation products from particle core to the surface was not rate limiting. Compared with other pyrolysis systems, which need smaller average particle size (DuPont et al., 2009), these results were surprising and may be explained with rate control by the transport of constituents in the heat carrier phase and the phase transfer step.

Solid product formation was monitored via elemental analysis of the carbon to oxygen ratio in biochar. Biomass carburation is shown in Fig. 3. Similar to liquid product formation, three steps of biochar formation were observed:

1. Initial phase of water discharge.
2. Carbonization and formation of condensibles.

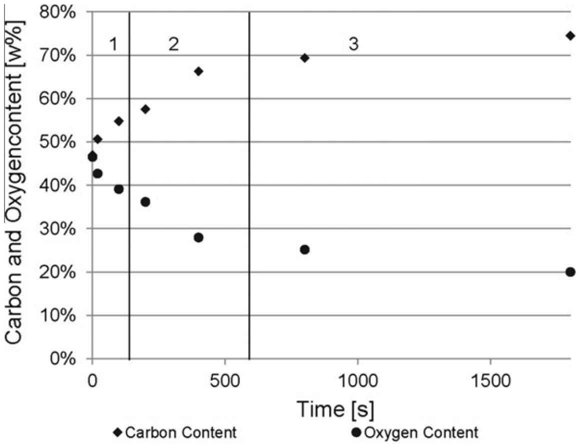

**Fig. 3.** Solid product formation.

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[1] Thermal conductivity detector. Gas chromatography–mass spectrometry.

[2] Simulated distillation with GC.

[3] Thermal conductivity detector.

[4] Attenuated Total Reflection Fourier Transform Infrared Spectroscopy.

[5] Environmental Scanning electron microscope, works on higher pressures (80-100 pa) then conventional Scanning electron microscopes, coating of samples is not necessary

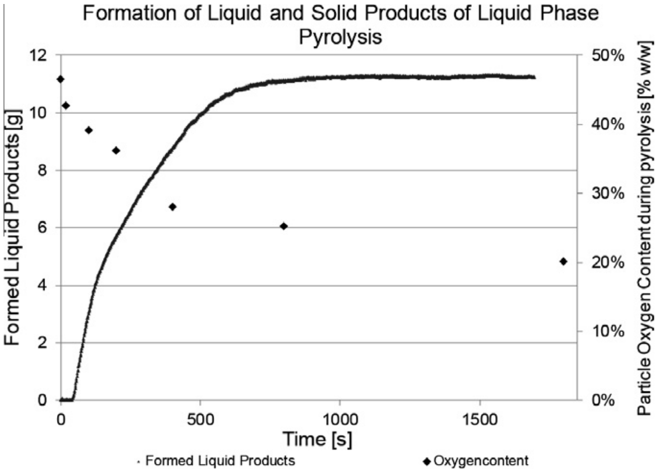

**Fig. 4.** Comparison of liquid and solid product formation.

3. Stagnant carbonization and formation of gaseous constituents.

While formation of condensibles was limited to phase 1 and phase 2, formation of gaseous products, preferably $CO_2$, dropped but did not stop. A clear view on the process was enabled by comparing liquid and solid product formation. Fig. 4 shows a comparison of liquid and solid products. The data showed correlation of formation of biocrudeoil and oxygen decline in biomass particles, indicating, that in liquid phase pyrolysis at $T = 350$ °C just oxygen rich biomass fractions were liquefied. As a consequence hemicellulose and cellulose were tending to be liquefied to a much larger extent than lignin.

To validate the proposed concept of favored carbohydrate liquefaction, ATR-IR spectra of biomass particles after distinct sequences of pyrolysis were compared. The ATR-IR spectra of native wood and after 400 s of pyrolysis do not differ significantly. As long as C–O bonds at a wavenumber of 1100 $\text{cm}^{-1}$ (Lin-Vien, 1991) were detectable, condensibles were formed. With vanishing C–O absorption liquefaction stopped and gas formation, caused by carburetion, was the driving process. It was possible to show the isochronous decrease of the C–O stretching vibration with termination of liquid product formation. The transformation of spruce wood into biochar was observed by SEM. During the first 400 s of pyrolysis the fiber like structures of native spruce wood were identifiable. After 400 s a structural change of the surface of biomass and a breakdown of the fibrous structure was monitored. Any rough fiber-like structures were observable and the overall image was similar to the final biochar structures. The remaining wood cell structure is finally sintered with partly melted middle lamella and primary wall. During this phase of pyrolysis lignin was highly enriched (Wagenführ, 1999; Saake and Lehnen, 2000). It indicated that lignin was almost stable in native wood structures and not split into oligomer and monomer fractions under liquid phase pyrolysis conditions.

**Table 2**
Massbalances of compounds.

| | Liquid CHO-products (%) | Solid residua (%) | Gas (%) | Water formed by reaction (%) |
|---|---|---|---|---|
| Cellulose | 34 | 29 | 16 | 21 |
| Ligin | 6 | 79 | 9 | 6 |
| Hemicellulose | 16 | 44 | 21 | 19 |
| Sprucewood | 26 | 40 | 17 | 17 |

**Table 3**
Simulation of overall pyrolysis.

| | Liquid CHO-products (%) | Solid residua (%) | Gas (%) | Water formed by reaction (%) |
|---|---|---|---|---|
| Simulated spruce | 21 | 47 | 16 | 16 |
| Spruce | 26 | 40 | 17 | 17 |

Table 2 shows the comparison of products for different feed, underlining the different role of constituents under thermal charge at $T = 350$ °C during liquid phase pyrolysis. Lignin was only sparingly liquefied, which matches with literature. Saikrishna et al. (2012) showed that 23% of lignin was liquefied at 500 °C. TGA records showed that more than 80% of lignin was left in the solid residue at 350 °C (Melligan et al., 2012).

With the results presented in Table 2 it was possible to simulate overall pyrolysis, enabling "construction" of product constituents of spruce wood. Therefore spruce wood was categorized, well specified according to literature (Nimz et al., 2000) by the three main components, lignin, hemicellulose and cellulose. Table 3 shows good accordance between simulation and experiments for water formed by reaction and the amount of gas formed during pyrolysis. These product streams originate in carbohydrate degradation as shown in Table 3. Simulation of liquid CHO-products and solid residues did not match with experiments because of minor lignin liquefaction. Seemingly lignin samples, isolated from kraft process, differ strongly from native lignin. Because of the interaction of lignin and carbohydrates in wood lignin rather tends to liquefaction than isolated lignin.

## 4. Conclusion

Liquid phase pyrolysis of spruce soft wood is an intermediate process, established between fast pyrolysis and torrefaction. The process is not very sensitive to particle size. Therefore intensive grinding and milling pre-treatment are not necessary for feed preparation.

During pyrolysis the lignin frame stayed almost substantially stable, sintering and shrinking was observed during carburetion.

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